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GASES IN METALS: I. THE DETERMINATION OF COMBINED NITROGEN IN IRON AND STEEL AND THE CHANGE IN FORM OF NITROGEN BY HEAT TREATMENT

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GASES IN METALS: I. THE DETERMINATION OF COMBINED NITROGEN IN IRON AND STEEL AND THE CHANGE IN FORM OF NITROGEN BY HEAT TREATMENT.

By Louis Jordan and F. E. Swindells.

ABSTRACT.

The only form of nitrogen determined in iron and steel by the usual methods of analysis is combined nitrogen, probably existing as nitride of iron, or of such minor constituents as manganese, aluminum, or titanium. The usual method of analysis of ferrous alloys for nitrogen is some modification of the Allen or acid-solution method. The use of glass-condenser tubes for the ammonia distillation and the determination of ammonia by the Nessler solution in the case of steels containing more than 0.1 or 0.2 per cent carbon are two sources of error. The second source of error frequently has been disregarded. In three classes of material evidence of the existence of two forms of nitrogen has been obtained, viz., in an electric furnace silico-manganese steel, a plain carbon steel from the outside surface of an autoclave plate, and in experimental electrolytic iron ingots. In these metals certain hardening heat treatments increased the amount of combined nitrogen. In three cases, viz., an open-hearth silico-manganese steel, the inside surface of the same autoclave plate, and in a second series of electrolytic iron ingots, this increase in combined nitrogen was not noted. It is probable that this increase is the result of the conversion of uncombined nitrogen to nitride nitrogen by heat treatment, and that nitrogen in two forms was present in the samples in which the increase took place.

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I. INTRODUCTION.

The only form of nitrogen ordinarily determined in steel is that combined as nitride, either of iron or of some of the other constituents. Tests for the presence of hydrocyanic acid or cyanogen on solution of steel in acid have been negative,[1] and all the combined nitrogen is generally regarded as being present as nitrides. It is readily conceived, however, that part of the nitrogen present is not combined but is either dissolved, adsorbed, or mechanically held. The nitrides to be considered as possibly present are those of iron, manganese, and silicon in an ordinary steel with some other possibilities in the cases of steels which have had additions of special deoxidizers or alloying elements such as aluminum, titanium, chromium, or similar metals.

II. THE ALLEN METHOD FOR COMBINED NITROGEN.

1. EARLIER MODIFICATIONS.

The usual method for the determination of the combined nitrogen in steel is a modification of that employed by A. H. Allen in 1880.[2] Allen dissolved the sample of metal in the form of drillings or millings in hydrochloric acid of specific gravity 1.11. When the solution was complete it was made alkaline with lime, the ammonia distilled off and determined with Nessler solution. H. Braune [3] employed this method with a few modifications. He specified that the solution should be filtered before introducing it into the distilling flask. He also used caustic soda in the distillation instead of lime.

In the 1918 edition of Blair's "Chemical Analysis of Iron and Steel" the Allen method is given with several modifications made by Langley. The chief change in the method is the treatment of the caustic-soda solution with a copper-zinc couple to remove nitrates and nitrites. Boussingault [4] had called attention to the fact that nitrates and nitrites in the solution during the distillation were partly reduced to ammonia by the ferrous hydroxide present.

Another method for the determination of the ammonia in the distillate was proposed in 1907 by Petren and Grabe.[5] This consisted in collecting the distillate in standard sulphuric acid, the excess acid being determined by the addition of potassium iodide-iodate solution, and titration of the liberated iodine with standard sodium thiosulphate solution. Hurum and Fay[6] have recently recommended the iodide-iodate modification of the Allen method for nitrogen determination.

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[1] H. Braune, Stahl und Eisen, 26, p. 1359; 1906.

[2] A. H. Allen, J. Iron and Steel Inst., 8, p. 181; 1880.

[3] H. Braune, Chem. Centralblatt, 75, Part II, p. 1167; 1904.

[4] Boussingault, Zeit. analyt. Chemie, 1, pp. 112–114; 1862.

[5] Petren and Grabe, Stahl und Eisen, 27, pp. 1700–1701; 1907.

2. TSCHISCHEWSKI'S MODIFICATIONS.

In 1915 Tschischewski[7] studied the Allen method and made several improvements. He used standard sulphuric acid to collect the distillate containing the ammonia and titrated the excess acid with standard alkali. He had previously objected to the use of the Nessler method for the determination of the ammonia in the distillate because of the probable presence of amines.[8] He also pointed out the probability of error from alkali dissolved from glass condensers, and warns against unprotected rubber stoppers in the distillation apparatus if the Nessler method is employed.

3. BLANKS.

As has been stated by Tschischewski, the size of the blank correction in this method is greatly influenced by the kind of condenser tube employed. Tests made at this bureau with glass condensers have given, after blank runs, an amount of alkali in the distillate equivalent to 0.0001 to 0.0002 g of nitrogen. The same solutions used in blank determinations with block-tin condenser tubes have given only 0.000015 g of nitrogen. The high blank with glass condensers is, however, quite constant and satisfactory duplicate results are obtained by carrying out two determinations on a given steel, using in one case the glass condenser and in the other the block-tin.

The blank correction when using glass condensers is larger than is desirable when it is considered that the combined nitrogen found by this method in a 5 g sample of steel lies between 0.0002 and 0.0007 g.

4. ERRORS FROM THE USE OF NESSLER SOLUTION.

The objection to the use of Nessler solution in the Allen method have been confirmed. A series of Bessemer steels was analyzed for combined nitrogen and the ammonia determined by both the acid-alkali titration and by the Nessler colorimetric methods.

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[6] T. Hurum and H. Fay, Chem. and Met. Eng., 26, pp. 218-222; 1922.

[7] N. Tschischewski, J. Iron and Steel Inst., 92, Part II, pp. 47-90; 1915.

[8] N. Tschischewski, Stahl und Eisen, 28, p. 397; 1908.

Except in the case of the 0.1 per cent carbon steel the Nessler method gave lower results than the titration method. The difference between the two values, the error in the Nessler determination, became greater the higher the carbon in the steel. The results of these analyses are shown in Table 1.

TABLE 1.—Comparison of Titration and Nessler Methods, Bessemer Steel Samples.

Approximate per cent carbon.	Per cent combined nitrogen.				Excess titration over Nessler.
	Titration.		Nessler.		
	Determination.	Average.	Determination.	Average.	
0.1	0.0133 .0126 .0123	0.0127	0.0132		
.2	.0105 .0107	.0106	.0090 .0097	0.0094	0.0012
.4	.0112 .0115	.0114	.0100 .0098	.0099	.0015
.6	.0094 .0095	.0095	.0076		.0019
.8	.0120 .0117 .0111 .0117	.0116	.0093		.0023

Many of the current texts on the analysis of iron and steel give directions for the determination of nitrogen by the Allen method with the use of the Nessler solution and do not call attention to Tschischewski's criticism of this procedure. The above results indicate that in steels containing 0.2 per cent carbon or over the error arising from the use of the Nessler solution is appreciable, and that titrimetric methods should be used for the estimation of ammonia in the distillate.

5. SOLUTION OF SAMPLES.

The solution of the sample of steel or iron is carried out in a small beaker with a cover glass heated on a steam bath. A number of determinations of nitrogen were made in which the solution of the sample was carried out in a closed vessel and the evolved gases led through a bubble tube containing hydrochloric acid, a procedure often recommended in this analysis. The acid in the bubble tube was combined with the acid solution of the sample in the flask and the ammonia determined in the usual manner. It was found that no higher results for nitrogen were obtained when the solution of the sample was made with provision for recovering ammonia in the evolved gases. Comparative results on the same materials dissolved by both procedures are given in Table 2.

TABLE 2.—Comparison of Methods of Solution of Sample.

Sample.	Evolved gases not washed in HCl.	Evolved gases washed in HCl.
	Per cent nitrogen.	Per cent nitrogen.
Bessemer steel	0.0121 .0125	0.0123 .0126
Electric arc-weld metal:		
A-8	.135	.132
A-10	.122	.119

Low results for nitrogen are, however, often obtained, if the solution of the sample is made in a beaker heated over a gas burner, on a hot plate, or on a sand bath instead of on the steam bath as described above.

6. METHOD AS USED BY THE BUREAU.

The method for combined nitrogen in use at the Bureau of Standards is essentially the Allen method with modifications, chiefly those by Tschischewski. (See foot note 7.) It was at first thought necessary to prepare special ammonia-free hydrochloric acid to be used in dissolving the sample, but it was later found that a fresh bottle of concentrated acid of the "c. p." grade, diluted with ammonia-free water to a specific gravity 1.11, usually gave a sufficiently low blank determination. The sample of steel or iron, 5 g in weight unless known to be very high in nitrogen,[9] is dissolved in 50 cm³ of this acid. While the solution is taking place 30 cm³ of the sodium-hydroxide solution prepared as directed by Blair and Langley,[10] one or two pieces of mossy zinc, and 400 cm³ of distilled water, are placed in the distilling apparatus. This distilling apparatus consists of a 1-liter Erlenmeyer flask connected with a condenser whose block-tin inner tube is bent downward at its upper end so as to form with a rubber-stoppered "carbon-filter" funnel a connection with the distilling flask, resembling a Kjeldahl connecting bulb (fig. 1). The alkaline solution in the flask is then boiled until 200 cm³ has distilled over. This distillate is discarded, the contents of the distilling flask are allowed to cool slightly, and the solution of the steel sample is introduced through a separatory funnel in the stopper of the distilling flask. The solution of the sample is not filtered. The beaker in which the solution of the sample took place and the separatory funnel are rinsed into the distillation flask with three 50 cm³ portions of ammonia-free water. The contents of the flask are then boiled until 200 cm³ of distillate are collected in 25 cm³ of 0.01 normal sulphuric acid. The adapter at the end of the condenser should dip into the standard acid or be connected with a receiver of a type which causes any escaping gas to bubble through the standard acid. After the distillation is complete the excess of sulphuric acid is titrated with 0.01 normal sodium hydroxide, using as an indicator one drop of a 1 per cent aqueous solution of sodium alizarine sulphonate. The end point is the complete disappearance of the clear green color or the first indication of brown. This method of determining the ammonia in the distillate is much superior to the method involving the use of Nessler solution, and probably as convenient and accurate as the iodide-iodate method.

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[9] For alloys containing 0.1 per cent nitrogen 2 g samples are used. With still higher nitrogen content, as in nitrogenized iron, the acid solution of the metal is diluted with ammonia-free water to a known volume and aliquot samples are taken which contain nitrogen equivalent to not more than 25 cm³ of 0.01 *N* acid.

[10] A solution of 300 g of sodium hydroxide in 500 cm³ of water and digested at 50° C. for 24 hours over a zinc-copper couple.

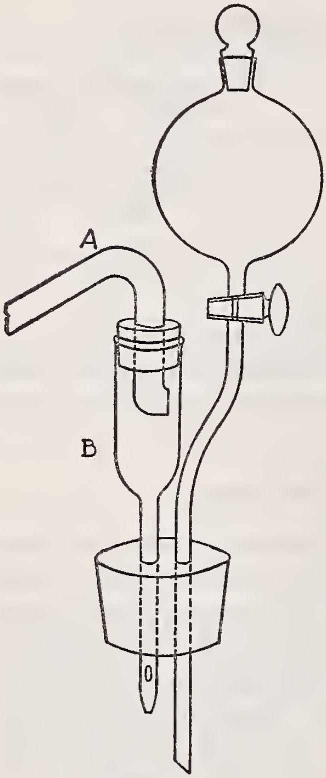

FIG. 1.

III. NITRIDES DETERMINED BY THE ALLEN METHOD.

A review of the properties of some of the nitrides possibly present in the steel indicates that iron nitride is readily and completely decomposed by dilute acids with the formation of ammonia.[11] Aqueous acids and alkalis have little effect on silicon nitrides;[12] fusion with alkali is required to convert their nitrogen to ammonia. Manganese nitride is decomposed slowly by water and more readily by acids;[13] it is rapidly decomposed by hot caustic alkali solutions with the formation of ammonia. Aluminum nitride is completely decomposed by hot alkaline solutions.[14]

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[11] G. J. Fowler, J. Chem. Soc., Trans., 79, pp. 285–299; 1901.

[12] L. Weiss and T. Englehardt, Zeit. anorg. Chem., 65, pp. 38–104; 1909.

[13] G. C. Henderson and J. C. Galletly, J. Soc. Chem. Ind., 27, p. 387; 1908.

[14] S. A. Tucker and H. L. Read, Trans. Am. Electrochem. Soc., 22, pp. 57–65; 1912.

Titanium nitride is insoluble in dilute acids but is decomposed in boiling potassium-hydroxide solutions.[15]

The nitrogen determined by the solution method is probably chiefly that present as iron and manganese nitrides. If the solution of the sample is not filtered before distillation it is possible that a large part or all of any nitrogen present as aluminum or titanium nitrides is also converted to ammonia by the boiling alkali solution during distillation. The nitrogen dissolved, adsorbed, or mechanically held in pores or blowholes can scarcely be expected to permit of determination by this procedure.

IV. TWO FORMS OF NITROGEN IN STEEL.

1. COMBINED NITROGEN INCREASED BY HEAT TREATMENT.

(a) SPRING STEELS.

In the course of some tests at the Bureau of Standards, on the behavior under heat treatment of two heats of silico-manganese spring steel, it was found that certain hardening treatments very noticeably increased the combined nitrogen in the electric furnace spring steel.[16] A steel of almost identical composition but made in an open-hearth furnace showed practically no increase in combined nitrogen under the same conditions of heat treatment.

The manufacturer's anaylses of these steels for the usual constituents gave the following results:

Steels.	C.	Mn.	P.	S.	Si.
A (electric)	0.53	0.77	0.022	0.014	2.09
B (open hearth)	.54	.77	.017	.022	2.03

Analyses of the rolled stock as received by the bureau showed in the electric steel nearly twice as much combined nitrogen as in the open-hearth steel (Table 3).

TABLE 3.—Combined Nitrogen in Spring Steels as Rolled.

Electric steel.		Open-hearth steel.	
Sample No.	Per cent nitrogen.	Sample No.	Per cent nitrogen.
A 16	0.0041	B 29	0.0019
	.0051		.0022
A 2	.0038	B 1	.0025
	.0047		.0031
	.0051		
Average	.0046	Average	.0024

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[15] O. Ruff and F. Eisner, Ber. deuts. chem. Ges., 41, p. 2252; 1908.

[16] H. J. French and L. Jordan, Discussion of paper by MacQuaid and Ehn. Paper No. 1163 issued with Mining and Met., May, 1922.

Samples of steels A and B, which had been given a regular hardening treatment, as practiced by spring manufacturers, and a normalizing quench followed by the regular hardening treatment, as well as a sample of steel A, which had been subjected to the normalizing quench only, were analyzed for combined nitrogen. In the "regular" treatment a hardening temperature of 900° C. (1,650° F.) was used. The normalizing quench was from a higher temperature, viz., 980° C. (1,800° F.).

The combined nitrogen in the open-hearth steel was not greatly, if at all, changed by the treatments given. In the case of the electric steel, however, either a normalizing quench or a normalizing quench followed by the regular treatment doubled the amount of combined nitrogen.

TABLE 4.—Influence of Heat Treatment on Combined Nitrogen in Spring Steels.

Treatment.	Electric steel.			Open-hearth steel.		
	Sample No.	Per cent nitrogen.	Average.	Sample No.	Per cent nitrogen.	Average.
As received			0.0046			0.0024
Regular hardening treatment	A 4	0.0065 .0068	.0066	B 2	0.0037 .0023 .0024	.0028
	A 5	.0061 .0064	.0063			
Normalizing quench	A 20	.0098 .0086	.0092			
Normalizing followed by regular treatment	A 31	.0109 .0095	.0102	B 19	.0025 .0035	.0030

It is difficult to believe that the heat treatment itself as carried out could increase the total amount of the nitrogen in the electric steel and make no change in the nitrogen in the open-hearth steel treated simultaneously. It seems probable, in view of the limitations of the solution method for nitrogen explained above, that there is no increase in the total nitrogen in the steel, but that a part or all of the nitrogen that was originally in a form not determined by this method was converted into a form that allowed of its determination.

Of interest in this connection is a patent granted to Krupp Akt.-Ges.,[17] which has claims based on the introduction of nitrogen into steel at temperatures below 580° C. in the form of solid solution as distinct from nitride of iron which is formed on heating above that temperature.

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[17] F. Krupp Akt.-Ges., Brit. Pat. 174580; Chem. Abst., 16, p. 1738, 1922.

(b) ELECTROLYTIC IRON TREATED WITH CALCIUM.

A series of ingots of electrolytic iron was next examined to determine if similar changes in combined nitrogen could be detected in iron free from the usual metallurgical impurities or alloying elements. These ingots had been prepared for another purpose, and to all but one (ingot No. 385) small amounts of metallic calcium had been added just before casting in a chilled mold. The melts were made in the high-frequency induction furnace in crucibles of 85 parts of magnesia and 15 of zircon. Combined nitrogen was determined in these ingots as cast. They were then given a heat treatment similar to the treatment which gave the greatest increase in combined nitrogen in the electric furnace spring steel, viz., a normalizing quench from 1,040° C. (1,900° F.) followed by a regular treatment from 910° C. (1,670° F.). In nearly every case there was a marked increase in the combined nitrogen. Four of these treated ingots were annealed at 950° C. (1,740° F.) for one-half hour and then cooled slowly over a period of about four hours. No very definite change in the combined nitrogen took place by this treatment. The slight differences observed were not uniform in direction.

TABLE 5.—Influence of Heat Treatment on Combined Nitrogen in Electrolytic Iron Ingots Treated with Calcium.[a]

Ingot No.	Per cent nitrogen as cast.		Per cent nitrogen after heat treatment.		Per cent nitrogen after annealing.	
	Determination.	Average.	Determination.	Average.	Determination.	Average.
380	0.0087 .0082 .0096	0.0088	0.0111 .0101	0.0106	0.0126 .0112	0.0119
381	.0015 .0030	.0022	.0029 .0037 .0051 .0059	.0044	.0029 .0032	.0030
382	.0030	....	.0050 .0054	.0052	....	....
383	.0015	....	.0040 .0042	.0041	....	....
384	.0028	....	.0042 .0037 .0037	.0039	.0042 .0030	.0036
385	.0016	....	.0036 .0038	.0037	.0024 .0021	.0022

[a] The calcium added was equivalent to 0.2 per cent in 380 and 381; 0.1 in 382; 0.03 in 383; 0.01 in 384. No addition was made to 385. The residual calcium in the ingots ranged from 0.04 to 0.003 per cent.

(c) AUTOCLAVE STEEL.

There was next examined a specimen of steel from an autoclave used for containing the catalyst and nitrogen-hydrogen gas mixture in the Haber process for nitrogen fixation. The gas mixture in this autoclave was treated at a pressure of 1,500 pounds per square inch and at a temperature of 500° C. Analyses of the inside and outside layers of the plate for the usual elements showed considerable decarburization of the inside layer.

Layers.	C.	Mn.	P.	S.	Si.
Outside	0.42	0.65	0.031	0.033	0.29
Inside	.14	.65	.032	.036	.29

Nitrogen determinations showed that the inside contained about 50 per cent more combined nitrogen than the outside. One sample of this plate was given the regular hardening treatment previously referred to in the case of the spring steels and another sample the normalizing quench followed by the regular treatment. There was a very marked increase in the combined nitrogen in the outside layer with both heat treatments. In the inside layer there was no change in the combined nitrogen.

TABLE 6.—Combined Nitrogen in Autoclave Steel as Influenced by Heat Treatment.

Layers.	As received.		Regular treatment.	Normalizing followed by regular treatment.	
	Per cent nitrogen.		Per cent nitrogen.	Per cent nitrogen.	
	Determinations.	Average.		Determinations.	Average.
Inside	0.0145 .0140	0.0142	0.0145	0.0146 .0156	0.0151
Outside	.0091 .0093	.0092	.0162	.0149 .0128	.0138

The failure of the combined nitrogen of the inside layer to be altered by heat treatment may possibly be explained by the fact that the conditions of service, viz., at 500° C. in the presence of hydrogen and nitrogen under pressure, were such that all the nitrogen, both originally present and diffusing into the plate, was converted during the operation of the autoclave into the form determined by the solution method. The outside layer of the autoclave plate was possibly at a lower temperature than the inside layer, a temperature below that necessary to convert to the nitride form the nitrogen diffusing from the interior.[18] A still more probable explanation is that the presence of hydrogen was necessary to cause all the nitrogen to form nitrides and that the outer layer of the plate was beyond the zone of hydrogen penetration as is idicated by the fact that the decarburization of the plate was limited to a narrow inner layer.

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[18] Compare the claims of the Krupp patent, footnote 17.

(d) FUSED ELECTROLYTIC IRON.

An attempt was then made to check the previous results obtained with the electrolytic iron. Three ingots of electrolytic iron were prepared in the high-frequency induction furnace and cast in the chilled mold. One was melted under quiet air in a crucible of 85 parts of magnesia and 15 parts of zircon. The other two were melted in pure magnesia crucibles, one being under quiet air and the other under a stream of pure nitrogen. These ingots were given the same heat treatment as the first electrolytic iron series, viz., a normalizing quench followed by a regular hardening treatment. No change in the combined nitrogen could be detected after the heat treatment.

TABLE 7.—Combined Nitrogen in Electrolytic Iron.

Ingot No.	Method of preparation.	Per cent nitrogen as cast.		Per cent nitrogen after heat treatment.	
		Determinations.	Average.	Determinaations.	Average.
388	MgO-Zircon crucible; under air	0.0033 .0030	0.0032	0.0031 .0030	0.0030
456	MgO crucible; under air	.0033 .0056 .0056	.0048	.0034 .0034 .0030	.0033
457	MgO crucible; under nitrogen	.0070 .0072	.0071	.0071 .0065	.0068

V. DISCUSSION AND SUMMARY.

1. ANALYTICAL METHOD.

The nitrogen in iron and steel, as determined by the Allen acid-solution method, is that present as combined nitrogen, probably as nitrides of iron, manganese, aluminum, and titanium. The original Allen method has been modified by previous critical studies with the elimination of certain errors. Three points in the analytical procedure are particularly emphasized in the present paper:

1. The solution of the metal sample may be made safely in a covered beaker heated on a steam bath. Solution of the sample with provision for washing the evolved gases to recover ammonia gives no higher results for nitrogen in the metal. Ammonia may be lost during the solution of the sample in acid if the reaction is hastened by heating over a free flame or on a hot plate or sand bath.

2. In carrying out the ammonia distillation in this method it is preferable to use condensers having block-tin inner tubes in

order that the blank correction shall not be of the same order of magnitude as the amount of nitrogen usually present in steels, a condition often existing when glass condensers are employed.

3. The ammonia in the distillate should be determined by a titrimetric method, such as the iodide-iodate or the sodium hydroxide method. Nessler's solution may be used for the colorimetric determination of ammonia in the distillate in the case of low-carbon or carbon-free iron alloys, but in the case of steels containing 0.2 per cent carbon or over the results obtained are appreciably in error.

2. FORM OF NITROGEN IN STEEL.

Evidence is given of the increase with heat treatment of the combined or nitride nitrogen in certain steels. Such an increase in combined nitrogen took place in an electric-furnace steel, but not in an open-hearth steel of identical composition and heat treated simultaneously. A similar increase took place in the outside layer of a plain carbon steel autoclave plate, but not in the inside layer of the same plate. Two series of electrolytic iron ingots melted in an induction furnace under air were examined for this change in nitrogen by heat treatment. An increase in nitride nitrogen was found in ingots of the first series, but not in those of the second series. The two series differed only in that small amounts of calcium had been added to the melts of the first series immediately before casting the ingots.

It is improbable that the observed increase in combined nitrogen in the above metals is due to nitrogen introduced during heat treatment since the electric and open-hearth steels were treated simultaneously, as were also both layers of the autoclave plate. The increase was found in one member of each pair but not in the other. In other words, the total nitrogen in these metals was not increased.

It is likewise improbable that the increase in nitrogen determined by the Allen method is due to the formation of iron nitride following the decomposition of nitrides not determined by this method of analysis, since this increase in combined nitrogen also took place in the first series of electrolytic iron ingots, which contained as the only impurity mere traces of calcium, the nitride of which is readily decomposed by acids.

It is to be concluded that nitrogen may be present in iron and steel in more than one form—as combined or nitride nitrogen and as uncombined nitrogen. The changes in the amounts of combined nitrogen are probably the result of conversion of free or uncombined nitrogen to nitride nitrogen. The free or uncombined form of nitrogen is not present in all samples of iron and steel, or may vary widely in amount.

The authors wish to acknowledge their indebtedness to H. J. French for carrying out the heat treatments of the metals examined, and to H. A. Bright for making the chemical analyses other than those for nitrogen.

WASHINGTON, July 27, 1922.

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